Published in final edited form as:

Appl Geochem. 2017 February ; 77: 142–157. doi:10.1016/j.apgeochem.2015.11.003.

Reversible adsorption and flushing of arsenic in a shallow, Holocene aquifer of Bangladesh

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Abstract

The spatial heterogeneity of dissolved arsenic (As) concentrations in shallow groundwater of the Bengal Basin has been attributed to transport of As (and reactive carbon) from external sources or to the release of As from within grey sand formations. We explore the latter scenario in this detailed hydrological and geochemical study along a 300 m transect of a shallow aquifer extending from a groundwater recharge area within a sandy channel bar to its discharge into a nearby stream. Within the 10–20 m depth range, groundwater ages along the transect determined by the ³H–³He method increase from <10 yr in the recharge area to a maximum of 40 yr towards the stream. Concentrations of groundwater As within the same grey sands increase from 10 to 100 to ~500 µg/L along this transect. Evidence of reversible adsorption of As between the groundwater and sediment was obtained from a series of push–pull experiments, traditional batch adsorption experiments, and the accidental flooding of a shallow monitoring well. Assuming reversible adsorption and a distribution coefficient, K_d , of 0.15–1.5 L/kg inferred from these observations, a simple flushing model shows that the increase in As concentrations with depth and groundwater age at this site, and at other sites in the Bengal and Red River Basins, can be attributed to the evolution of the aquifer over 100–1000 years as aquifer sands are gradually flushed of their initial As content. A wide range of As concentrations can thus be maintained in groundwater with increases with depth governed by the history of flushing and local recharge rates, without external inputs of reactive carbon or As from other sources.

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Keywords

Arsenic; Bangladesh; Adsorption; Hydrology; Groundwater age dating; Push–pull tests

1. Introduction

The spatial variability of arsenic (As) in groundwater pumped from shallow Holocene aquifers of South and Southeast Asia has been well documented by various research teams at dozens of sites over the past decade and half (e.g. BGS/DPHE, 2001; Harvey et al., 2002; McArthur et al., 2004, 2008; Polizzotto et al., 2008; Kocar et al., 2008; Postma et al., 2007, 2012; van Geen et al., 2003a). A commonly observed feature is an order-of-magnitude increase of As concentrations in groundwater within the upper 30 m of an aquifer. The underlying reasons for this feature, and why the increase in groundwater As with depth can change considerably from one location to the other, are still poorly understood. The question needs attention, because tens of millions of villagers throughout the affected region continue to rely on shallow wells as their main source of drinking water. Without a quantitative understanding of the mechanisms as to how and why As increases with depth, doubts will remain concerning how long a shallow well that once tested low for As can continue to be used for drinking and cooking (McArthur et al., 2010; Fendorf et al., 2010).

In the much smaller number of detailed As studies that include profiles of bomb-produced ^3H and its radiogenic daughter ^3He , groundwater ages relative to the time of recharge inferred from these measurements also increase with depth (Klump et al., 2006; Postma et al., 2007, 2012; Stute et al., 2007). One of these studies, which included paired profiles of both As and ^3H – ^3He ages for 6 sites separated by a few kilometers in Bangladesh, showed that As concentrations rose more rapidly with depth at sites where groundwater ages also increased faster with depth (Stute et al., 2007). This relationship was subsequently interpreted as an indication that the rate of flushing of a Holocene aquifer determined the amount of exchangeable As remaining in the sediment and, therefore, also As concentrations in groundwater (Aziz et al., 2008; van Geen et al., 2008). Another study, conducted at 4 sites across a 10-km transect in Vietnam, has since shown that the depth gradient of As concentrations in shallow aquifers can also be a function of sediment age (Postma et al., 2012).

The common theme underlying these and many other studies is the extent to which the release of As to groundwater in Holocene aquifers is regulated by the availability of reactive carbon and/or exchangeable As (Harvey et al. 2002; Zheng et al., 2005; Mladenov et al. 2015). For both reactive carbon and exchangeable As, either transport from a shallow source that affects a shallow aquifer or *in situ* reaction from sediment within the aquifer has been invoked for different sites (Polizzotto et al., 2008; Neumann et al., 2010; Desbarats et al., 2014; Harvey et al., 2006; Mladenov et al., 2009; Mailloux et al., 2013). The goal of our study was to test the limits of internal As release by thoroughly characterizing a site that seemed hydrologically tractable and had groundwater As depth profiles that varied markedly over a very short distance. The observations from the site were integrated with a simple model which assumes that reversible adsorption and the extent of flushing are the key

parameters. We demonstrate the relevance of this new understanding by applying the same model to other well-studied aquifers in the Bengal and Red River Basins.

2. Methods

2.1. Study site

The study site (90.63° E, 23.79° N) in a small village located 25 km northeast of Dhaka Araihaazar, Bangladesh, is a sandy point bar where a cluster of low-As concentrations (at <50 m depth) was documented in a blanket survey of private wells (van Geen et al., 2003b; Weinman et al., 2008). Sediment incubation experiments were previously conducted using material from the site (Radloff et al., 2008). The land surface of the site is characterized by a sandy, raised area in the village with a gradually thickening silty-clay layer extending beneath the adjacent agricultural fields, which are bordered by a small stream (Fig. 1). Weinman et al. (2008) described several of the fine scale patterns (10^1 – 10^2 m) of local fluvial subsurface stratigraphy that are found within Araihaazar. Using their classification scheme, the study site described here can be characterized as having near-surface sandy outcrops underlain by clean sands (Facies A or B), which are characteristic of channel bars and levees formed under high flow regimes (Weinman et al., 2008).

The stratigraphy of the area was confirmed with a surface electromagnetic conductivity survey and extensive coring (Aziz et al., 2008). The surface sediments at the site have a lower EM conductivity (and therefore are coarser) than the average sediments in the region. Recharge is therefore likely to be concentrated in particularly coarse areas found in and along the border of the raised sandy village. The surface elevation decreases about 2 m from the village to the stream; depths across the transect are referenced throughout the paper relative to one location, the base of a concrete utility pole in the village, and were determined using a clear water-filled tube. From the surface to 10 m depth, the sediment is a silty sand. A thin (<5 cm) clay layer located at approximately 10 m depth was identified while drilling at several locations. Below 10 m the sandy aquifer is physically homogeneous and no other extensive clay lenses were identified. A thick grey clay layer (>5 m) provides a lower confinement of this aquifer and is found between 30 and 35 m depth. On the basis of these observations, groundwater was expected to flow from the elevated sand bar, presumed to be the main recharge area, to the zone of discharge in a local stream at a distance of 300 m (Fig. 1).

2.2. Monitoring wells

2.2.1. Installation and sample collection—The village to stream transect includes 6 locations that are labeled by referring to their distance (in meters) from the nearby stream. The main transect includes four monitoring locations which are in a line from the village to the stream (K240, K150, K60 and K5). Up to 5 wells were installed at each location with 1-m screens centered at approximately 7, 10, 15, 20 and 30 m depth. At two additional locations located off of the main transect, 3 wells were installed in the shallow aquifer at 7, 10 and 15 m depth (K80W and K40E). Additional wells were installed within a 0.25 km² area surrounding the transect, totaling 41 monitoring wells distributed across 24 locations.

Profiles of groundwater and sediment were also obtained by needle-sampling (van Geen et al., 2004).

Groundwater samples for metal and anion analysis were collected at 18 monitoring wells biweekly from December 2006 through 2009. For the remaining wells, samples were collected every 3 months from February 2008 through 2009. The most extensive sampling campaigns took place in March 2007, 2008 and 2009. Groundwater was collected using a submersible pump (Typhoon, Proactive) after purging the well for at least 3 well volumes. During collection, groundwater was continuously monitored for temperature, pH and conductivity using a multiparameter water monitoring probe in a flow cell (MP 556 from YSI, Inc.), while dissolved oxygen was measured using 0–40 ppb kits (Chemetrics). Samples for metal and anion analyses were filtered inline through 0.45 μm syringe filters (Whatman 6753–2504) and collected in 20 mL plastic scintillation vials; the samples for metal analysis were also acidified to 1% HCl (Optima) in the field.

2.2.2. Field protocols—Dissolved Fe(II) was measured in the field using ferrozine (Stookey, 1970). The alkalinity of groundwater was determined within a day after sampling (Gran, 1952). As speciation was determined by difference by filtering groundwater in the field through columns that retain As(V) but not As(III) (Meng et al., 2001). Ammonia concentrations were measured on the day of sampling by colorimetry (Sorzano, 1969).

2.2.3. Water level measurements and loggers—Groundwater levels were monitored in 41 wells and at two locations within the stream, from the bridge and in an L-shaped pipe near K5, over a 2 year period from March 2007 to 2009. Manual water level measurements were taken biweekly for 18 wells and the stream locations from December 2006 to November 2009, and approximately every 3 months from February 2008 to November 2009 for all locations. In order to prevent floodwater intrusion, 1.5 m-long galvanized iron (GI) extensions were added to the wells located in low-lying areas during the monsoon season. Pressure transducers (Leveloggers, Solinst) were deployed in 8 wells and recorded pressures every 20 min from March or May 2007 through 2009. All water levels are reported relative to the base of the concrete utility pole in the village. Pressure transducer data were corrected for barometric pressure changes, as recorded by a pressure transducer in the village, to determine the water height above the transducers.

2.2.4. Water analyses—Groundwater As, Fe, Mn, P, and S and major ion concentrations were measured by high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) and has a precision of $\pm 3\%$ (1σ , Cheng et al., 2004). Anion concentrations were measured by ion chromatography (IC) using a DIONEX-500 IC system, following the standard protocol of EPA method 300. Methane concentrations were measured on samples collected in 50 mL glass crimp vials using blue butyl rubber septa (Bellco) with no headspace and poisoned with 0.1 mL of saturated HgCl_2 solution (Fisher Scientific) to prevent degradation. The samples were analyzed approximately one month after collection by introducing an N_2 gas headspace and letting the water reequilibrate with the headspace. The re-equilibrated headspace was then analyzed by gas chromatography with a flame ionization detector (FID). As(III) concentrations were measured in select samples using differential pulse cathodic stripping voltammetry (DPCSV) using an Eco Chemie Autolab

voltammeter and a Metrohm 663 VA electrode stand (Brinkmann Instruments) (He et al., 2004; Jung and Zheng, 2006).

Stable water isotope samples were collected in 60 mL glass bottles with polyseal caps from all shallow (<15 m) wells in March 2008 and the deeper wells (20 and 30 m depth) in March 2009. These samples were analyzed at the Environmental Isotope Laboratory of the University of Waterloo with a precision of 0.1‰ ($\delta^{18}\text{O}$) and 1‰ ($\delta^2\text{H}$). Groundwater for radiocarbon analysis was collected in 250 mL glass bottles with polyseal caps and was poisoned with 0.2 mL of saturated HgCl_2 .

2.2.5. Groundwater dating—Samples for ^3H were collected in 125 mL glass bottles with polyseal caps, while samples for ^3He were collected in 16 cm long, 1-cm- OD copper tubes (volume approximately 16 mL) crimped sealed on the ends with stainless steel clamps (Weiss, 1968). Analysis of ^3H in groundwater was performed using the ^3He ingrowth technique (Bayer et al., 1989; Clarke et al., 1976; Ludin et al., 1998). For samples collected in 2007, the full suite of noble gases were measured by mass spectrometry (Stute et al., 1995), while only He and Ne measurements were performed on the samples collected in 2008 and 2009, also by mass spectrometry (Ludin et al., 1998). The precision of the ^3H measurements is ± 0.05 at 1.0 TU and the detection limit is 0.05 TU. The precision of noble gas measurements is typically $< \pm 2\%$ (standard error) and the precision of He and Ne only measurements 0.5–1%. Analyses of $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ in dissolved inorganic carbon (DIC) were performed at the NOSAMS facility at Woods Hole Oceanographic Institution following standard protocols with a precision of 0.1% (Elder et al., 1998).

2.3. Sediment collection and analysis

2.3.1. Sediment collection—Intact sediment cores were recovered at regular intervals from the surface until approximately 15 m depth within a few meters of monitoring nests K240, K150 and K60. The traditional sludger method (Horneman et al., 2004) created a borehole to a specified depth and a manual push soil corer (AMS 424.45) was then used to recover a core from the bottom of the borehole. The top few centimeters of each core were discarded to ensure that only undisturbed material was analyzed. At greater depths, core recovery was poor and drill cuttings were therefore collected instead. The drill cuttings are biased towards the larger grain sizes, as some of the clay and silt particles are removed in the drilling process (Horneman et al., 2004). Needle sampling was also used to collect groundwater and sediment slurries from several depths to compare with the core and cuttings (van Geen et al., 2004). Sediment collected from all methods were used to characterize the sediment, but only cores and cuttings were used in the adsorption experiments.

2.3.2. Field measurements—Drilling logs recorded during the installation of the 24 well nests provided a physical description of the sediment lithology of the shallow aquifer. Sediment color was quantified on the basis of diffuse reflectance spectra at about half of the well locations and at nine locations along the northern stream bank. The slope of the diffuse spectral reflectance of the sediment between 530 and 520 nm, reported in units of percent reflectance per 10 nm (%/10 nm) and referred to here as R without units, was used as an indication of Fe speciation in the solid phase (Horneman et al., 2004; van Geen et al., 2006).

The reflectance of the drill cuttings was measured every 1.5 m from the surface to the lower (35 m depth) clay layer.

2.3.3. Sediment extractions—Three separate extractions in (a) water, (b) 1M phosphate and (c) 1.2N hot HCl were performed on the cores, needle samples, and drill cuttings within one day of collection in the field to target readily desorbed As, adsorbed As and As associated with less crystalline Fe oxyhydroxides, respectively. Prior to extraction, samples were stored in the sampling container (plastic core liner or needle sampling tube) in air tight mylar bags with oxygen adsorbents (Sorbent Systems) to minimize oxidation. Sediment samples were well mixed before aliquots were taken for each extraction. For (a) water extraction, ~1 g of wet sediment was mixed with 10 mL of distilled water that had been bubbled with N₂ for 1 h and was then crimped sealed in glass bottles. The water extracts were collected 31 days later by drawing the water from the serum bottles using a syringe and filtered immediately. Some solutions were also passed through Meng et al. (2001) columns for As speciation. For (b) phosphate extractions, ~1 g of wet sediment was mixed with 10 mL of a 1 M sodium phosphate solution with 0.1 M of L-ascorbic acid and shaken for 24 h, after which the solution was passed through a 0.45 µm syringe filter (Jung and Zheng, 2006; Keon et al., 2001). For (c) HCl extractions, ~1 g of wet sediment was mixed with 10 mL of 1.2 N HCl (Optima) and warmed to 100° C for 1 h, after which the solution was allowed to settle and a portion of the supernatant was collected. Arsenic concentrations in all three extraction types were analyzed by HRICP-MS following a protocol similar to the one used for groundwater. Iron speciation of the sediment was determined by analyzing the HCl extraction using the ferrozine method (Horneman et al., 2004).

2.3.4. Bulk sediment analyses—Sediment cores were collected in 5 locations for detailed grain size analysis and XRF analysis. Using approximately 30 g of sediment, the coarse fraction (sand) analysis was completed following a modified version of the USGS East Coast Sediment Analysis Procedures to separate the sediment into three size fractions: >150 µm, 63–150 µm, and <63 µm (Poppe et al., 2000). Two handheld X-ray fluorescence devices (Innov-X Systems Alpha model with a Hewlett–Packard iPAQ. PocketPC and an Innov-X Delta Premium for a subset of samples) were used for analyzing the bulk sediment composition. With the Alpha instrument, measurements were collected using the 60-s standard test and a 30–60-s light elements test in soil mode. Bulk concentration of As were measured using the more sensitive Delta Premium instrument for 300 s. Standardization of the instruments was checked with two USGS or NIST soil reference samples approximately once every twelve measurements.

2.3.5. As speciation by X-ray absorption spectroscopy (XAS)—Synchrotron X-ray absorption spectroscopy (XAS) for As was performed on beamline 11–2 at the Stanford Synchrotron Radiation Laboratory in California using sediment samples preserved in glycerol. Arsenic XANES spectra were collected using the protocol described in Jung et al. 2012. All data averaging, normalization, and linear combination fitting was done with SIXPack software (Webb, 2005). Arsenic XANES fits were performed on normalized spectra. Arsenate and arsenite adsorbed on ferrihydrite (100 g As/kg ferri-hydrite, pH 7) were used to represent adsorbed As(V) and As(III), and orpiment (As₂S₃) was used to

model arsenic sulfides. Arsenopyrite (FeAsS), which contains As(-I), was also used in fitting but was not required to fit any spectra. The estimated errors in least-squares fitting are determined using SixPack software, and were determined to be ~3% for the As XANES fits.

2.4. Batch adsorption experiments

2.4.1. Preparation—Batch As adsorption experiments were conducted within a day of collecting groundwater and sediment. Groundwater was collected into 150-mL glass serum bottles with no headspace and was allowed to over flow into a bucket, before capping with gas impermeable blue butyl rubber septa (Bellco) and crimp sealed. Sediment was stored in air-tight mylar bags with oxygen adsorbents (Sorbent Systems). The batch samples were mixed in a glove bag (Sigma Aldrich Z555525), which was flushed with ultra-high purity nitrogen gas and monitored with an oxygen indicator strip (Becton Dickinson) to maintain close to anaerobic conditions (less than 1% O₂). Sediment was removed from the cores in the glove bag and thoroughly mixed in a re-sealable bag before dispensing 4–6 g of sediment into individual glass vials. Then 11 mL of groundwater was added to the vials and were capped with butyl rubber septa and crimp sealed while still in the glove bag. A range of volumes of an As(III) spike (1000 mg/L) were added to samples from all depths to increase the As concentration up to 15,500 µg/L, while an As(V) spike (1000 mg/L) was added to samples taken from 7 to 12 m only. One sample from 7 to 12 m, at each location, also received an addition of phosphate (approximately 4000 µg/L P) and no As addition. The spike solutions of 1000 mg/L As(III), As(V) and P were freshly prepared using reagent grade NaAsO₂, NaHAsO₄·7H₂O and NaH₂PO₄·2H₂O, respectively.

2.4.2. Water and sediment analyses—After 31 days, groundwater from the adsorption experiments was sampled through the septum with a syringe to prevent exposure to oxygen and filtered immediately through a 0.45 µm syringe filter for analysis by ICP-MS. As(III) concentrations in the adsorption experiments were determined using Meng et al. (2001) columns as well as differential pulse cathodic stripping voltammetry (DPCSV) using an Eco Chemie Autolab voltammeter and a Metrohm 663 VA electrode stand (Brinkmann Instruments) (He et al., 2004; Jung and Zheng, 2006). The sediment from the batch adsorption experiments underwent a sequential extraction to remove the sorbed As. First, 10 mL of the phosphate solution was added to the sediment in the batch vials, crimp sealed and shaken for 24 h. Next, the sediment was moved to larger vials with 50 mL of 1.2 N HCl (Optima) and warmed to 60° C for 24 h, but not shaken. The supernatants from these two extractions were analyzed for As content only.

2.5. Push-pull experiments

2.5.1. Preparation and sampling—The push–pull tests were conducted at two well nests, K40E and K80W (Fig. 1). Four experiments lowered the groundwater As concentration surrounding the well and an additional experiment injected higher As groundwater into a well with less As (Table 1). Each experiment required two wells; one functioned as the source and the other well received groundwater. Bromide was added as a conservative tracer to assess dilution and was dynamically mixed with the source water as it was pumped from the source well directly into the receiving well. The source well was pumped with a locally-available irrigation pump and a high-pressure gradient piston pump

(Cole–Parmer) was used to introduce the concentrated Br solution into the flow from the irrigation pump. Approximately 14 L/min of source water was mixed in-line with 2 mL/min of the concentrated solution for an injected Br concentration between 50 and 60 mg/L. Approximately 1000 L of the modified groundwater was then immediately injected into the receiving well. Groundwater samples were collected over the following 15 days and monitored for bromide and alkalinity in the field. Each experiment is referred to by the name of the receiving well.

Three desorption tests were performed at K40E where low As groundwater (7 µg/L) from a well screened in a deeper aquifer (at 45 m depth) was injected into shallow wells screened at 7, 10 and 15 m, with groundwater As concentrations between 200 and 400 µg/L. In the K40E – 7m test, 1005 L of groundwater with 7 µg/L of As and 56.0 mg/L Br was added to a well with an initial groundwater As concentration of 233 µg/L. The K40E – 10 m test added 1034 L of the same groundwater with 50.9 mg/L of Br into a well with 343 µg/L of As, while K40E – 15 m test added 812 L of water with 62.6 mg/L of Br into a well with 412 µg/L of As. The injection rate was slower for the K40E – 15 m test compared to the other experiment, with the source water entering at 6 L/min and the tracer added at 1 mL/min.

Two tests were performed at K80W using three wells screened in the shallow aquifer (screened at 7, 10 and 15 m, respectively). The only adsorption test that was conducted as part of this study injected 1012 L of water from K80W – 15 m with 204 µg/L of As and 58.4 mg/L of Br into K80W – 7m with an initial groundwater As concentration of 71 µg/L and is referred to hereon as the K80W – 7 m test. Subsequently, a desorption test injected 1010 L of water from 10 m depth with 97 µg/L of As and 53.8 mg/L of Br into the well at 15 m with an initial groundwater As concentration of 204 µg/L, and is referred to as the K80W – 15 m test.

2.5.2. Modeling—Analysis of the push–pull experiments requires a simple box model to address both the spatial distribution and kinetic limitations of adsorption in the aquifer; the same approach is described in Radloff et al. (2011). This model assumes homogenous plug flow during injection (push) and the step-wise withdrawal (pull). Only samples moderately affected by mixing, as indicated by $Br/Br_0 > 0.7$, were used for model fitting. Adsorption was modeled as reversible, kinetically-limited Langmuir sorption.

The box model was used to evaluate two potential adsorption scenarios. The first and simplest adsorption scenario, also known as the single porosity model, assumes that all adsorption sites are equally accessible. The second scenario sets the Langmuir adsorption constant, K , to the distribution coefficient (K_d) derived from the batch adsorption experiments and assumes two types of adsorption sites with different accessibility, but the same distribution partitioning (Wood et al., 1990; Harvey and Gorelick, 2000; Hellerich et al., 2003). Rapid adsorption occurs on one type of site and diffusion limits the rate of adsorption onto the second type of site. The fraction of rapidly adsorbing sites (x_f), the adsorption constant (K), the adsorption rate constant (k_f), and the diffusion rate (k_{diff}) are all determined by fitting the undiluted samples from all five experiments to a single set of parameters. The best model fit was determined by minimizing the sum of the squared residuals between modeled and measured groundwater As concentrations.

2.6. Models of groundwater age and sediment flushing

2.6.1. Groundwater age profile in a simple aquifer—The idealized Vogel model for a homogeneous aquifer presented by Schlosser et al. (1989) is used to estimate vertical flow velocities from the vertical profiles of groundwater ages derived from ^3H – ^3He data. The model predicts a logarithmic increase in groundwater ages with depth that is inversely proportional to the rate of recharge and the groundwater age at depth z is described using:

$$t(z) = \frac{z_{\max}}{v_0} * \ln \left(\frac{z_{\max}}{z_{\max} - z} \right) \quad (1)$$

where v_0 is the vertical flow velocity and $z_{\max}$ is the thickness of the aquifer, which is assumed to be constant. The vertical flow velocity is simply the recharge rate divided by the porosity and is also assumed to be constant.

Assuming a uniform rate of recharge of a two-dimensional aquifer, the model predicts that the profile of groundwater age is independent of its location within a two-dimensional aquifer; thus the vertical age profile is constant. Using this simplified approach, knowledge of specific flowpaths, and the specific horizontal and vertical velocities associated with them, is not needed. Thus, the groundwater age can be used to approximate the extent of flushing without specific knowledge of the flowpath.

2.6.2. Advection dispersion model—van Geen et al. (2008) used a simple model to predict the impact of gradually flushing a shallow aquifer of its original content of exchangeable As by recharge by water without As. We use the same model here to estimate how the relationship between groundwater As concentrations and groundwater age could evolve over geologic time due to flushing. Using the same one-dimensional advection dispersion model, the relationship between groundwater age and As concentration can be evaluated for any K_d , which are converted to retardation factors, R , using the aquifer bulk density (2.65 g/cm^3) and porosity (0.3). The model solution (from van Genuchten and Alves, 1982) calculates the groundwater As concentration at a given distance along the flowpath (x) at a specified time (t) since flushing began assuming that the recharging water contains no As and is:

$$C(x, t) = C_i \left[1 - \frac{1}{2} \operatorname{erfc} \frac{(Rx - vt)}{2(DRt)^{\frac{1}{2}}} + \frac{1}{2} \exp\left(\frac{vx}{D}\right) \operatorname{erfc} \frac{(Rx + vt)}{2(DRt)^{\frac{1}{2}}} \right] \quad (2)$$

where C_i is the initial groundwater As concentration, v is the advection velocity, and D is the hydraulic dispersion coefficient. The C_i was set to $1000 \text{ } \mu\text{g/L}$ as an upper limit to what has been observed in Bangladesh. A new aspect of the modeling is that the velocity and flowpath distance (x) were estimated at specific depths in the aquifer using the estimated vertical flow velocity derived for this site using the model of Vogel described by Schlosser et al. (1989). The scaling of v and x is proportional using the Vogel model, therefore the model solution is the same for a long, fast flowpath or a short, slow flowpath if the groundwater ages are the same. Hydraulic dispersivity was estimated to be 10 m, which is representative of sandy

aquifers across spatial scales of ~100 m (Gelhar et al., 1992). Hydraulic dispersion is estimated to be the vertical flow velocity multiplied by the dispersivity. Groundwater As concentration were predicted over a range of years after flushing began and for a range of distribution coefficients.

3. Results

3.1. Water levels

The hydrology of the site is dominated by the monsoon that induces a nearly 5 m rise in hydraulic head and submerges almost half of the study area for several months each year (Fig. 2). Changes in groundwater levels typically lag behind the stream, in both the rising and falling phases. Groundwater levels are lower than the stream level at the beginning of the dry season (December) and are drawn even lower due to irrigation pumping. Stream levels rise faster than groundwater levels in April and May and reach their maximum difference of 1 m. Flood water arrives in July and equalize stream and groundwater levels. Most of the agricultural fields at Site K are submerged while the village remains above the flood water. As the flood water begins to recede in October, groundwater levels remain higher than stream levels until the start of the dry season. In the dry season, the stream is frequently dammed to form ponds for aquaculture and is largely stagnant. Net flow direction at the site was estimated using manual measurements made biweekly in ten wells located along the transect from K240 to the stream. The lowest annual average water level was recorded in the village and water levels increased towards the stream (Table 2, Supplementary Material Figure A1.1). The implication is that net flow under current conditions is directed from the stream towards the village instead of the anticipated opposite direction. Biweekly water levels measured in the wells located on the other side of the stream mirror the main transect; they are a similar amount above or below the stream water levels at the same times of year (Supplementary Material Figure A1.3). This indicates that the stream hydraulically separates the groundwater on either side at all times of the year.

3.2. Groundwater ages

The age of groundwater relative to recharge in the study area was determined on the basis of ^3H and ^3He concentrations for a total of 33 wells (Fig. 1). All wells screened at less than 20 m depth contained detectable ^3H , an unambiguous indication of recharge since the input reached a maximum in the 1950s and 1960s due to atmospheric testing of nuclear weapons. Tritium was also detected in some wells in the 20–30 m depth range, primarily those within and closest to the village (Supplementary Material, Table A2.1). With the exception of two samples, groundwater ages calculated from paired ^3H and ^3He measurements are consistent with the original content of ^3H (measured in TU) of water derived from these measurements and a simple model of ^3H input based on the historical record of tritium content in precipitation in Asia, indicating that little mixing is occurring (Stute et al., 2007 and Supplementary Material Figure A2.2).

The ^3H – ^3He data show that groundwater from wells within the village is particularly young (<5 yr). At the other end of the spectrum, the oldest (~35 yr) groundwater containing ^3H is located primarily near the stream both on and off the main transect. The groundwater in two

shallow wells on the other side of the stream (KW15 and KW32) is younger and consistent with the observation from the water levels that the stream is a hydrologic boundary (Supplementary Material Figure A2.1). Vertical profiles in the northern portion of the transect show an increase in age with depth and towards the stream (Fig. 3B). At K240, K150, and K60, the age of groundwater is between 1 and 12 yr in the 7–10 m depth range and converges to 30–35 yr at ~20 m depth. Groundwater ages are more homogeneous and average 30–40 yr at K5 and K40E in the southern portion of the aquifer. The ^{14}C content of DIC, reported in FMC (fraction modern carbon), is lowest in the deeper wells located closer to the stream (Supplementary Material, A2.2). In five wells, ^3H – ^3He data alone cannot provide an estimated age.

The presence of younger groundwater in the village and fields and older groundwater closer to the stream indicate long-term flow from the village towards the stream, as anticipated based on the topography of the site but opposite to the direction indicated by recent water-level measurements. The presence of younger groundwater at K150 than K240 at 10 and 15 m suggests that the original assumption that water flows in the north-south direction from K240 to K150 was also incorrect.

3.3. Groundwater chemistry

The composition of groundwater was measured in March 2007, 2008 and 2009 in the 25 monitoring wells at 6 locations along the transect. By and large, the composition of groundwater did not vary substantially from one sampling occasion to the next (Supplementary Material, Figure A3.2). Results from the most recent sampling are presented for all wells, which was March 2009 for most parameters. In wells located within the village, As levels typically remain below 50 $\mu\text{g/L}$ As. At nest K240 located within southern portion of the village, groundwater As concentrations rise to nearly 100 $\mu\text{g/L}$ at 15 m. Groundwater As concentrations increase further towards the stream and reach a maximum of 600 $\mu\text{g/L}$ between 15 and 30 m (Fig. 3A). At shallower depths (<15 m), As concentrations as high as 400 $\mu\text{g/L}$ are reached at a distance of 50 m from the stream (at K40E and K80W) but decrease to 200 $\mu\text{g/L}$ at closer to it (K5). With the exception of the shallowest well at K240 within the village, which contains only 2 $\mu\text{g/L}$ As, over 90% of the As in groundwater is present as As(III) (Supplementary Material, Table A3.1).

Concentrations of other groundwater constituents confirm the reducing nature of the aquifer indicated by field measurement of dissolved O_2 (<0.025 mg/L) and ORP (–12 to –182 mV), even in the most rapidly recharged northern portion of the transect. Ground-water Fe concentrations generally increase with depth and range from 0.3 to 19 mg/L (Fig. 3C). Groundwater Mn concentrations range from 0.2 to 3.7 mg/L and peak between 10 and 15 m (Supplementary Material, Figure A3.1). Groundwater SO_4 concentrations were highest at K240 within the village location (40 mg/L at 10 m) and undetectable (<0.1 mg/L) near the stream (Fig. 3D). Concentrations of ammonium increase from the village to the stream, with a peak concentration of ~150 μM at 7 m depth at K60, before decreasing to 80 μM at well K5 closest to the stream (Fig. 3E). In contrast, groundwater P ranges from 0.3 to 2.2 mg/L without a systematic trend with depth or distance from the stream (Fig. 3F). Methane was detected in shallow (<15 m) wells at several locations along the transect and increase to 3.1

mg/L toward the stream (Supplementary Material, Figure A3.1). The deeper wells were not sampled for methane, however numerous bubbles were observed in groundwater from deeper samples near the stream, suggesting particularly high concentrations (20 and 30 m at K60 and K5).

Measurements of ^2H and ^{18}O in groundwater can distinguish different sources of recharge of the aquifer. The isotopic composition of shallow (<15 m) groundwater at Site K was comparable to that of precipitation in the area; the deuterium excess ($\delta^2\text{H}-8*\delta^{18}\text{O}$) of precipitation is approximately 10 and shallow wells had values ranging from 7.8 to 12. This indicates that much of the shallow groundwater is derived from rain or flood waters during the monsoon rather than from ponds or irrigated fields during the dry season (Supplementary Material, A3.3).

3.4. Flooded-well observations

Unusually high flood waters evidently flowed into the 10 m well at K150 on July 31, 2007 (Fig. 4A). A rapid increase in water level was recorded by the levellogger installed in this well as the stream water entered the wells through the small holes in the well cap used to ensure the well remained at barometric pressure. On August 3, 2007, the stream water intrusion was stopped after a 1.5 m GI pipe extension was installed and a sample was collected. This well was routinely sampled every 2 weeks, however, and groundwater composition changes induced by this unintended push-pull experiment were therefore documented. The time series shows that groundwater As concentrations were relatively steady and averaged 350 $\mu\text{g/L}$ before the intrusion and then decreased to 18 $\mu\text{g/L}$ (Fig. 4B). Groundwater Fe concentrations also decreased from 9 mg/L to 1.3 mg/L, Mn concentrations from 2.0 to 0.2 mg/L, P concentrations from 1.0 to 0.1 mg/L and major cation concentrations decreased from 3.5 to 0.9 meq/L. Conversely, sulfate concentrations increased from 0.2 mg/L to 3.7 mg/L and then to 4.9 mg/L, before decreasing again. Over the next 10 weeks, concentrations of all groundwater constituents gradually returned to levels recorded before the perturbation. A similar observation was also made at the 7 m well at KW16, which also had a levellogger installed. However only samples collected every two months are available for this well (Supplementary Material, Figure A3.2).

3.5. Sediment chemistry

The shallowest depth of the sandy portion of the aquifer, defined here by a proportion of sand in sediment cores >50%, ranges from 5 to 9 m along the transect (Fig. 5A). The silty-clay layer that caps the aquifer thickens and becomes more dominated by clay away from the village and eventually extends to 10 m depth near the stream (Supplementary Material, Figure A4.3). Bulk concentrations of Fe in aquifer sands measured by XRF vary from 10 to 35 g/kg without showing any systematic spatial pattern (Fig. 5B). The ratio of Fe(II) to total Fe in the HCl-extractable fraction of the aquifer sands averages 0.7 ± 0.1 , with values < 0.5 recorded in only a few sandy intervals. In the surficial clay and silt layer, several values < 0.25 were measured at K240 and K150 (Fig. 5C). These patterns are broadly consistent with reflectance data obtained on fresh cuttings showing that Fe oxides are reduced throughout the sandy aquifer, with the exception of a few sandy intervals <10 m deep at K240 (Supplementary Material, Figure A4.1).

Bulk As measurements in aquifer sands measured by XRF indicate concentrations ranging from 1 to 10 mg/kg and averaging 4.3 ± 2.3 mg/kg (Fig. 5D). With the exception of two intervals, concentrations of P-extractable As in aquifer sands are about a factor of three lower (Fig. 5E). Arsenic speciation was determined using X-ray absorption near edge spectroscopy (XANES) in six sediment samples and indicate a large fraction of As bound to sulfide at K240 (47, 34 and 33% at 10, 15 and 20 m, respectively), less at K150 (16% at 10 m), and none at K60 (10 and 20 m, Fig. 5F). With the exception of the 10 m interval at K240, about 60% of the remaining arsenic in aquifer is As(III), with As(V) not exceeding 40% anywhere (Supplementary Material, Figure A4.1).

3.6. Batch adsorption experiments

The degree to which As adsorbs to aquifer sands was quantified with batch experiments at 3 locations (K240, K150 and K60) and at 5 depths (7, 10, 15, 20, 30 m) at each location. Of the 15 sediments selected for the batch experiments, only the sands from 7 m at K240 were less reduced ($\text{Fe(II)/Fe} \sim 0.4$) than the other locations where Fe(II)/Fe ranged from 0.6 to 0.9. In all 15 experiments, additions of either As(III) or As(V) up to 15,500 $\mu\text{g/L}$ were readily adsorbed within a month. Most samples show little to no dampening of adsorption due to site saturation. Dissolved Fe concentrations in the incubation bottles remained near ambient concentrations of 0.4–16 mg/L for the duration of the experiment (Supplementary Material, Table A5.5). This indicates the batch adsorption experiments were not compromised by the precipitation of Fe oxides, which could have occurred with a large influx of oxygen.

We use the additions up to 8000 $\mu\text{g/L}$ As to infer the most representative K_d s because of the non-linear response in some of the samples for the highest addition of 15,500 $\mu\text{g/L}$. We focus on the experiments conducted with aquifer sands collected by coring at 7 and 10 m depth rather than cuttings because the grain size distribution is unbiased in the cores and the material is less likely to have been exposed to atmospheric oxygen during sample collection. In the less reduced sediment of K240-7 m, the K_d was estimated to be 2.8 L/kg, while in the 5 more reduced samples the K_d averaged 1.1 ± 0.2 L/kg. There was no discernible difference in the amount of added As(III) or As(V) adsorbed on aquifer sands from these samples (Supplementary Material, Figure A5.2). The distribution coefficients obtained for cuttings at 15, 20 and 30 m depth are comparable, ranging from 1.0 to 2.7 L/kg, and show no clear spatial trends (Table 3). Overall, the range of measured K_d s was small, with an average of 1.7 ± 0.6 L/kg for the 14 reduced intervals with $\text{Fe(II)/Fe} > 0.5$.

At the end of the adsorption experiments, the speciation of As was determined in groundwater, and in the P-extractable fraction. The speciation of As in groundwater was dominated (>85%) by As(III), even in the incubation bottles that were spiked with As (V). P-extractions at the completion of the experiment recovered 50–70% of the newly adsorbed As and was dominated by As(III) in all cases, including batches spiked with As(V) (Supplementary Material, Figure A5.3).

3.7. Push-pull experiments

The push–pull experiments were designed to observe changes in groundwater As concentrations after a perturbation of the presumed adsorptive equilibrium in the field rather than with an incubation bottle containing a diluted sediment slurry. The Br tracer added during the push phase was used to calculate expected As concentrations in the absence of exchange between groundwater and aquifer sediments. In the push–pull experiments where lower As groundwater was injected, As concentrations after injection (<100 h) were higher than predicted from conservative mixing, indicating a release from the sediment (Fig. 6). For tests at K40E, groundwater with 7 µg/L of As was added to wells containing between 233 and 412 µg/L. After 24 h, groundwater concentrations ranged from 101 to 127 µg/L (31–43% of the original concentration) and after 100 h from 134 to 216 µg/L (44–58%, Fig. 6A–C). For the test at K80W- 7 m, water with 97 µg/L of As was added to a well with 204 µg/L. After 24 h, the groundwater As concentration was 136 µg/L, or 67% of the original concentration, and remained at this concentration after 100hr (Fig. 6E). The one experiment where groundwater with higher than ambient As concentrations was injected, groundwater with 204 µg/L As was pumped into a well containing 71 µg/L. By 24 h, the As concentration was 135 µg/L and after 140 h had dropped to 114 µg/L, indicating that about 70% of added As was retained in the aquifer (Fig. 6D). Groundwater Fe, SO₄ and P concentrations were also measured during the push–pull tests, even though the experiments were designed to minimize differences between source and receiving wells (Table 1). When ambient concentrations differed from the injected groundwater, the expected adsorption or desorption of F and P was observed (Supplementary Material, A6).

Using the box model of Radloff et al. (2011) and assuming all sites are equally accessible (fraction of rapid sites, x_f = 100%), a reasonable fit to all the undiluted samples from all five experiments is obtained for K of 0.17 L/kg and an adsorption rate constant (k_f) of 0.02 hr⁻¹ (Fig. 6). Predicted As concentration reach a plateau after about 100 h even though the measured concentrations continue to increase. The fit improves when more rapid adsorption is modeled to occur on a small subset of readily accessible sites and slower adsorption occurs on the remaining less accessible sites. The main reason is that the dual porosity model predicts a gradual rebound of As concentrations over the entire duration of the experiment. Under this scenario, K has to be assumed and a value of 1.5 kg/L, based on adsorption experiments for the more reduced sediments, was selected. Fitting yields a proportion of interior sites of 94% (x_f = 6%) and a k_f of 1.24 hr⁻¹ and a k_{diff} of 0.0006 hr⁻¹, respectively. The proportion of less accessible sites is at the high end the 70–80% range reported for less accessible sites in similar sandy aquifers (Wood et al., 1990; Harvey and Gorelick, 2000; Hellerich et al., 2003). Both the single- and dual-porosity models underestimate the decline in As concentrations attributable to adsorption following the single experiment where groundwater with a higher than ambient As concentration was injected (Fig. 6). Measured As concentrations decreased to 125 µg/L in 50 h, while the modeled concentrations were higher (~150 µg/L).

4. Discussion

4.1. Recent reversal in flow direction

Seasonal reversal of groundwater flow due to monsoon flooding has been observed in other areas of Bangladesh, Cambodia, and Vietnam where elevated As levels in shallow groundwater pose a serious health threat (Harvey et al., 2006; Benner et al., 2008; Larsen et al., 2008; van Geen et al., 2013). Benner et al. (2008) confirmed in Cambodia, where groundwater is not used for irrigation, that the net flow of water through river banks is determined by elevation and leads from groundwater aquifers into rivers in non-arid regions. This is the flow direction indicated at our study site by groundwater ages increasing from <10 to 30–40 years along the transect (Fig. 4). Water level measurements averaged over 2007–09, however, indicate net flow in the opposite direction, i.e. from the river into the aquifer (Table 2). Such reversals have been attributed elsewhere in Bangladesh and in Vietnam to large-volume pumping for irrigation and municipal water supply, respectively (Harvey et al., 2006; van Geen et al., 2013).

Transient decreases of 5–15 cm in water levels at one well located near an irrigation pump (KW16, Supplementary Material, Figure A1.5) indicate that irrigation pumping for growing rice during winter probably contributed to flow reversal at the study site. At the height of the irrigation season, the lowest water levels were recorded in the fields south of our study village where three irrigation wells are located (Supplementary Material, Figure A1.3). On average, however, the lowest water levels were observed within the village and therefore to the north of the rice fields, where there are only domestic hand-pumps. The observations therefore suggest an additional perturbation, likely to be the large cotton-spinning mill built between 2003 and 2006 on the other side of the stream, which started operating around the time when water level surveys were initiated (Supplementary Material A1.5). The factory discharges water pumped from a deeper aquifer into the stream. The discharge volume is not known, but interviews of local staff indicate that the factory pumps an estimated 400,000 L/day from the deeper aquifer (R. Mozumder, personal communication). This amount of water could have significantly raised the level of the stream during the dry season, when it does not flow and local farmers build temporary dams across it to retain water for aquaculture. The net flow reversal is therefore probably very recent and should not have affected the composition of water near the stream. This is confirmed by both the groundwater age of 35 yr and the precipitation-like stable isotope signature in the shallow wells at K5, which is similar to that of groundwater to the north rather than river water subject to evaporation during the dry season.

4.2. Exchange of As between groundwater and aquifer sands

A previous push–pull experiment conducted in a shallow aquifer of Bangladesh composed of grey sands, combined with selective extractions of As and Fe from sediment at the same site, has been interpreted as an indication that sediments are saturated with As once groundwater concentrations are greater than 100 µg/L (Harvey et al., 2002; Swartz et al., 2004). In contrast, As adsorption occurred readily in our adsorption push–pull experiment, in which groundwater with an As content of over 200 µg/L was injected into a well with an initial concentration of 97 µg/L of As, indicating that the sediment was not saturated. In

addition, our batch experiments show that the adsorption capacity of grey sands is high and not sensitive to the redox state of As. Similar observations were reported by Jung et al. (2012) using grey riverbank sands. Itai et al. (2010) also conducted a series of batch adsorption experiments and saw no evidence of saturation for groundwater As concentrations less than 1000 µg/L. These results suggest that a linear distribution coefficient, K_d , adequately represents both adsorption and desorption of As in reducing aquifers at ambient groundwater As concentrations.

The push–pull and batch adsorption experiments, combined, constrain the distribution coefficient, K_d , for As in reducing aquifers to the 0.15–1.5 L/kg range. The high end might over-estimate the extent of As adsorption, because the sediment–water ratio used in the batch adsorption experiments was lower than in the actual aquifer (Limousin et al., 2007). Even a K_d of 1.5 L/kg is a factor of 2–3 lower than the value of predicted from 1 M P-extractions of As from grey Bangladesh sediment for the southern portion of the transect (3–15 L/kg) and results from previous studies across the Bengal Basin (van Geen et al., 2008 and Itai et al. 2010), suggesting that P-extractions over-estimate the proportion of exchangeable As in aquifer sands. The push–pull derived K_d using the single-porosity model of 0.15 L/kg provides a plausible lower bound for As adsorption. The limited range of adsorption affinity observed in both the batch and push–pull experiments suggests that the characteristics that most influence As adsorption do not vary substantially within this aquifer, even though groundwater redox conditions vary from suboxic (sulfate-reducing) to methane-generating. Adsorption of As is known to be sensitive to Fe mineralogy (Jung et al. 2012, and references therein) and sediment Fe(II)-total Fe ratios were indeed comparable throughout the aquifer, with the exception of some of the shallowest intervals (Fig. 5). The observations also suggest that the degree of As adsorption remains stable soon after reducing conditions are established.

The extent of partitioning of As between aquifer sands and groundwater has significant practical implications. The kinetics of adsorption and desorption estimated from the push–pull experiments are sufficiently fast that equilibrium is expected under normal flow conditions. Assuming a K_d of 1.5 L/kg, the redistribution of As from a hot spot into a low-As area by irrigation pumping would be delayed by a factor of ~14 relative to the movement of groundwater. This delay would provide considerable protection for the large number of villagers who have relied on shallow low-As wells to lower their exposure. If instead the partitioning of As between groundwater and aquifer sands is determined by a distribution coefficient closer to 0.15 L/kg, aquifers would be flushed of their initial content of exchangeable As over time scales of decades instead of centuries, but the migration of plumes of high As concentrations would be more rapid, slowed by a retardation factor of only ~2. In addition, under intensive irrigation pumping scenarios, adsorptive equilibrium may not be reached, and therefore the effective K_d may be more similar to the lower estimate. This lower estimate is consistent with early indications of flushing and movement of As in reducing aquifers reported from West Bengal (McArthur et al., 2010).

4.3. Low As concentrations due to precipitation as arsenic-sulfide

The several-fold lower dissolved As concentration from the northern portion of the transect is not likely due to adsorptive equilibrium alone. With the exception of the shallowest, less-reduced sample from K240, the K_d s derived from the batch adsorption experiments with grey sands from within the village are not different from the values obtained in the southern portion of the transect. This uniformity contrasts with the 10-fold higher K_d s calculated from the P-extractions and the low ambient ground-water As levels in the northern portion of the transect. The simplest explanation is precipitation of As-sulfides, which was previously proposed as a mechanism for suppressing the release of As to groundwater under reducing conditions (Polizzotto et al., 2006; Lowers et al., 2007; Buschmann and Berg, 2009). The data indicate that sulfide precipitation at our study site retains considerable quantities of As, on the order of 0.4–1.7 mg/kg (based on total As estimates from XRF), and presumably limits the As available for desorption and flushing from the sediment. Within the northern portion of the transect, this mechanism is supported by the detection of As-sulfide in aquifer sands at two points along the transect where sulfate concentrations are elevated (5–50 mg/L) and the lack of As-sulfides at one location where sulfate levels are also undetectable (Fig. 5). The association also suggests that the supply of sulfur is a limiting factor for the formation of As-sulfides. High groundwater sulfate levels have been observed in both sandy, rapidly recharged areas and clay-capped, slowly recharged areas of Araihaazar (Stute et al., 2007; Dhar et al., 2008; Aziz et al., 2008). Recharge may therefore not be the primary source of sulfur to groundwater. An alternative source is decaying organic matter contained in the fine-grained sediment layer (Schroth et al., 2007; Planer-Friedrich et al., 2012).

4.4. Evolution of the arsenic-depth relation with time

The estimates of adsorption equilibrium and flushing rate of the aquifer allow us to create a simple yet plausible model to predict the evolution of the vertical distribution of As in groundwater over time. In addition to the distribution coefficient, K_d , the model requires an initial concentration of exchangeable As after an aquifer becomes reducing and sands have turned grey. The value selected is somewhat arbitrary and could vary with the depositional history of the sediment. An upper limit for groundwater As concentration of 1000 µg/L As in groundwater is set by the few reports of higher concentrations in South and Southeast Asia. This amount corresponds to concentrations of 0.15–1.5 mg/kg for exchangeable As for K_d of 0.15–1.5 kg/L, respectively. The assumed initial concentration of exchangeable As, 1.5 mg/kg for the K_d of 1.5 kg/L scenario, is below the current bulk concentration of ~3 mg/kg and similar to the P-extractable concentration of 1 mg/kg at the study site (Fig. 5). Both of these concentrations are likely to overestimate the exchangeable As concentrations today but, on the other hand, could already have been substantially reduced from initial conditions by flushing.

To apply the flushing model, groundwater velocity is first estimated from the profiles of groundwater ages (Fig. 7A). Current groundwater As concentrations are then matched with modeled flushing times, starting from the time when conditions became sufficiently reducing. Assuming first a K_d of 1.5 L/kg, the profile of groundwater age and As concentrations in the southern portion of the study transect resembles predictions for a vertical flow velocity of 0.25 m/yr and a flushing time of about 500 yr (Fig. 7B). When the

recharge velocity is doubled to 0.5 m/yr to match the profile of groundwater ages in the northern portion of the transect, the otherwise identical model predicts groundwater As concentrations that are considerably higher than most of those observed. Assuming instead a K_d of 0.15 L/kg, observed As profiles across the entire transect are more closely matched by the model if a much shorter flushing time of 50 yr is assumed (Fig. 7C). Sediment dating of the site by Optically Stimulated Luminescence (B. Weinman, unpublished) indicates that the shallow aquifer was deposited 4000 years ago in the village (at K240) and was deposited only 400 yrs ago closer to the stream (at K60). However, the available dates cannot rule out the possibility that the upper 7 m of the aquifer was deposited only 50 instead of 500 years ago and therefore do not help constrain the estimated range of K_d s.

4.5. Impact of flushing on Groundwater As elsewhere

The vertical age and As profiles from a dozen other sites across South and Southeast Asia can be used to evaluate whether the parameters estimated for the present site are more broadly relevant. Vertical flow velocities estimated for other 4 other sites in Araihaazar using the Vogel model, which range from 0.7 to 5 m/yr, agree with previously estimated recharge rates of Stute et al. (2007) that do not consider aquifer thickness (Table 4, Fig. 7D). At 4 sites in the Red River basin of Vietnam, reported vertical flow velocities derived from ^3H – ^3He dating, ranging from 0.25 to 0.5 m/yr, are consistent with the profiles generated using the Vogel model (Postma et al., 2012, Table 4, Fig. 7F). The model is also applied to a few other sites in Bangladesh and West Bengal, India, where vertical flow velocities ranging from 0.5 to 2 m/yr (i.e. 0.15–0.6 m/yr recharge) have been estimated (Klump et al., 2006; McArthur et al., 2010). Finally, the flushing model is applied to a site in Cambodia where particularly slow recharge of 0.04 m/yr was derived from a groundwater flow model and could not be verified with ^3H – ^3He dating (Polizzotto et al., 2008; Kocar et al., 2008; Benner et al., 2008). Model results for the additional sites in Bangladesh, West Bengal and Cambodia are reported in the Supplementary Material (Section A7).

The flushing model is used primarily to predict where ground-water As concentrations rapidly increase with depth. Even for a distribution coefficient, K_d , of 1.5 L/kg, the high recharge rates at Sites C and F in Araihaazar suggest that very little time (50–75 yrs) was required to reduce concentrations to their present level (Fig. 7B); no higher As concentrations are observed within the shallow aquifer at these sites. At Sites A and B within Araihaazar, the model correctly predicts a rapid increase in As with depth with slower recharge and a flushing time of about 200 yr for K_d of 1.5 L/kg (Fig. 7E). For a K_d of 0.15 L/kg, the required flushing time would be about an order of magnitude lower, which seems unlikely given the depositional history of the area (Weinman et al., 2008).

Using again a K_d of 1.5 L/kg in the Red River basin, the model confirms that sediment deposited 500–1000 yr ago would be nearly flushed of their As content (Fig. 7G). The duration of flushing for the more recently deposited sediments at H –transect was estimated to be 200 yr (Fig. 7G) based on the observation that peak groundwater As concentrations occur between 10 and 15 m depth. These flushing times are in line with estimates of sediment ages of from 500 to 6000 yrs at these sites (Postma et al., 2012). The match with independently dated sediments suggest that the lower K_d of 0.15 L/kg is less likely for this

site. Flushing times for a few other sites in the Bengal Basin range between 250 and 1000 yrs for different recharge rates. Finally, the model indicates that the groundwater As distribution and very slow rate of recharge in Cambodia require >5000 yr of flushing, which is consistent with age dating of the sediment at the site (Supplementary Material, A7). Taken together, the idealized flushing model predicts flushing times that are in line with known estimates of sediment ages across a wide range of settings for a distribution coefficient, K_d , of about 1.5 L/kg rather than the lower value inferred from the single porosity model applied to the push-pull data.

4.6. Evolution of the As-age relation over time

The idealized flushing model provides a context for revisiting the observation of Stute et al. (2007) that groundwater As concentration generally increased with groundwater age across several sites within Araihaazar. According to the flushing model, differences in hydrology across sites are in principle normalized by this representation. The new data from Site K clearly indicate a more gradual increase in As concentrations with age than at the other sites in Araihaazar (Fig. 8A). The scatter in the As-age relationship does not increase markedly, however, when data are added from the limited number of sites elsewhere in the Bengal Basin and the Red River delta where groundwater has been dated (Fig. 8B).

Using what appears to be the more widely applicable K_d of 1.5 L/kg, the flushing model is used to illustrate the effects of ground-water velocity and aquifer age. The results show the effect of different flow velocities on the groundwater As-age relationship is detectable but modest (Fig. 8A). Much more significant is the effect of flushing time (and therefore sediment age) (Fig. 8B). The slope of groundwater As-age relationship shifts over flushing time, such that less flushed aquifers may have high As concentrations in relatively young groundwater, while high As concentrations are only found in older groundwater in more flushed aquifers. Flushing gradually reduces the range of As concentrations across the range of groundwater ages (Fig. 8B) and deepens the location of the peak As concentration. The model cannot claim to explain all the available observations, but it indicates that a wide range of As concentration should be expected for a given groundwater age and that this variability may reflect an aquifer's age and extent of flushing.

5. Conclusion

A number of studies from both Bangladesh and Cambodia have suggested that the release of As during Fe reduction in near surface sediments is the primary contributor to groundwater As concentrations deeper within the aquifer, with little exchange of As occurring further downstream. The push-pull tests conducted at our study site clearly demonstrate that the aquifer instead responds rapidly to perturbations in groundwater concentrations by either desorbing or adsorbing As. The tests also indicate the presence of a dispersed source of As throughout the aquifer. Adsorption modeling constrains the distribution coefficients for As to between 0.15 and 1.5 L/kg. The high end of this range is consistent with a series of batch adsorption experiments and with the estimated age of the aquifer formation based on an idealized model of As flushing. Despite its limitations, the idealized flushing model appears to be consistent with shallow groundwater As profiles elsewhere in the Bengal and Red River basins where groundwater has been dated and locations are subject to different

recharge rates and extent of irrigation pumping. While external sources such as ponds, wetlands, and fine grained deposits may be important sources of As or reactive carbon at these sites, they are not necessary to explain the broad distribution of As in a way that is consistent with the range of recharge rates encountered in low-lying fluvial-deltaic aquifers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Columbia University and the University of Dhaka's research in Araihaazar has been supported since 2000 by NIEHS Superfund Basic Research Program grant NIEHS 5 P42 ES010349. Additional support for these experiments was received from Barnard College and the Earth Institute at Columbia University. The authors thank H. C. Siu for the grain size analysis (Bronx Science High School). This is Lamont-Doherty Earth Observatory contribution number 7953.

Appendix A

Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2015.11.003>

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Fig. 1. Site map with private well data and EM survey

A satellite image of the study area is shown; the village is located under the tree cover and the stream crosses the southern portion of the image. 24 well locations are shown and differentiated by their use. Light purple triangles show multi-well nests with up to 5 wells, screened at 7, 10, 15, 20 and 30 m. Dark purple triangles show wells locations where the push-pull experiments were conducted. Orange triangles show single well location where groundwater samples were collected and water levels were measured. Results of the EM survey are shown (EM conductivity reported in mS/m). Arsenic concentrations measured in private wells are shown in colored circles, ranging from blue for low As (<10 $\mu\text{g/L}$) to black for high As (>100 $\mu\text{g/L}$) wells. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Seasonal hydrograph

Biweekly water levels were measured from December 2006 until June 2009 and then reduced in frequency to every 2 months. Data shown is from the bridge monitoring location (in blue) and K240 (in red). Water levels in the aquifer (at K240) were also recorded every 20 min with a pressure transducer (shown in orange). Dashed green lines indicate relative elevation of the fields. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Selected Groundwater Properties at Site K

Vertical profiles extending from the surface to about 30 m depth are shown for 6 locations.

Color indicates distance from stream, changing from blue in the village to green to red to black near the stream bank. Six parameters are shown here: As in µg/L (A), ^3H - ^3He Apparent Age in years (B), Fe in mg/L (C), SO_4 in mg/L (D), NH_4 in µM (E) and P in mg/L (F). Unfilled symbols in the apparent groundwater age indicate samples with evidence of groundwater mixing and are not included in later analyses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Flood Water Perturbation

Unusually high flood waters (shown as stream height relative to the well) breached the well casing at K60–10 m resulting in floodwater entering the wells on July 31, 2007 the next sample was collected on August 3rd and a 1.5 m extension pipe was added to the well to prevent further intrusion. Groundwater concentrations of As, Fe, Mn, P and the major cations all decreased, while sulfate concentrations increased over this time. Concentrations returned to normal 10 weeks later.

Fig. 5. Selected Sediment Properties at Site K

Vertical profiles extending from the surface to about 30 m depth are shown for 5 locations. Color indicates distance from stream, changing from blue in the village to green to red to black near the stream bank. Sediment collected by coring are shown with solid markers and are connected by a line in the sandy portion of the aquifer. Sediment collected from needle sampling or as drill cuttings are shown as open markers. Six parameters are shown here: percent sand (>150 μm , by weight) (A), Fe in g/kg by XRF (B), Fe(II)/Fe from HCl-extractions (C), As in mg/kg by XRF (D), PO₄-extractable As in mg/kg (E) and percent As-sulfides by XANES (F). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Push-pull time series for As

Groundwater As concentrations are shown for the five push-pull tests. Dashed lines indicate expected concentration if there was no reaction (estimated from change in [Br]); samples with significant dilution (e.g. $[\text{Br}]/[\text{Br}]_0 < 0.7$) are shown as unfilled diamonds. Best fits are shown for two scenarios – a single porosity model (red dash, $K = 0.17$), and a dual porosity model, where K was set to 1.5 L/kg (blue dash). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Groundwater As and Age profiles with depth

Measurements and model results for Site K are shown in Panels A, B and C; for other sites in Araihaazar in D and E (Stute et al. 2007); and for Vietnam in F and G (Postma et al. 2012). Measured groundwater ages and modeled age profiles based on the Vogel model are shown in A, D and F. Groundwater As concentrations and estimated concentration based on the idealized flushing model for a K_d of 1.5 L/kg are shown in B, E and G, with model results for a K_d of 0.15 L/kg shown only in panel C.

Fig. 8. Groundwater As and Age Relationship

Results from Site K and other sites in Araihaazar (Stute et al., 2007) are shown in Panel A. The original observed As- age relationship (dotted line) is shown along with idealized flushing model results for various groundwater velocities using a K_d of 1.5 L/kg and a flushing extent of 500 years (colored lines). Results from other sites (Postma et al., 2012; Klump et al., 2006 and McArthur et al. 2010) are included in Panel B along with idealized flushing model results for flushing extents of 250, 500 and 750 years using a groundwater velocity of 0.5 m/yr and a K_d of 1.5 L/kg. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1

Groundwater properties of push-pull wells.

Well	Purpose	Depth m	As ug/L	Fe mg/L	P mg/L	SO ₄ mg/L	Mn mg/L	pH	As after Experiment	
									~400 h	~2months
K40E -7m	Recv. Well	8	233	12.0	0.9	0.3	3.1	6.6	159	207
K40E -10 m	Recv. Well	11	343	8.7	1.1	0.1	0.7	6.7	218	310
K40E -15 m	Recv. Well	16	412	8.7	0.9	0.2	0.6	6.8	348	415
K40E - 45 m	Source for K40E tests	45	7	8.9	1.4	0.3	0.1	6.7		
K80W -7m	Recv. Well	8	71	1.2	0.2	2.2	3.4	6.7	102	89
K80W - 10 m	Source to K80W -15 m	11	97	6.7	1.1	0.2	1.3	6.7		94
K80W - 15 m	Recv. Well, Source to K80W -7m	17	204	8.8	0.7	0.2	3.1	6.9	183	217

Dissolved As, Fe, P, SO₄, Mn and pH are reported for the wells used in the push-pull experiment. As concentrations at 400 h and 2 months after the push-phase are also included.

Table 2

Annual average of manually-measured water levels.

Well nest	Water level (m)				
	K240	K150	K60	K5	Stream
Well depth					
7m	-2.87	-2.83	-2.80	-2.81	-2.76
10 m	-2.87	-2.85	-2.81		
15 m	-2.87	-2.84	-2.85		

Average water level determined from biweekly manual measurements collected from February 2007 to 2009. Depth of water table is reported relative to one location in the village.

Table 3

Measured K_d s from experiments and sediment extractions.

Push-pull tests		Model results				
Single porosity		0.17				
Dual porosity		1.50				
Batch methods		Core material		Drill cuttings		
Adsorption isotherm		7m	10m	15m	20m	30m
K240		2.8	1.2	2.2	2.7	1.2
K150		1.1	0.8	2.4	1.7	1.0
K60		1.4	1.0	2.0	2.1	2.4
Phosphate-extraction						
K240		539.4	33.1	15.3	8.4	10.8
K150		8.5	7.9	12.4	4.6	3.2
K60		12.4	2.3	1.4	1.3	2.6
K80W		13.6	8.2	4.9	–	–
K40E		1.2	1.4	2.2	–	–
Water-extraction						
K240		8.3	2.8	0.8	1.1	0.9
K150		0.8	1.4	1.6	1.0	0.7
K60		3.0	2.1	0.7	0.3	0.8

Distribution coefficients, K_d , determined in the push-pull experiments, batch adsorption isotherms and in the phosphate and water extractions are reported in L/kg.

Table 4

Velocity and flushing extent estimated for other sites using the idealized flushing model.

Site	Aquifer thickness (m)	Est. Vertical velocity (m/s)	Flushing time (yr)	Reference
Araihazar, Site K	25	0.25 to 1	500	This study
Araihazar, Site A	10	0.7	200	Stute et al., 2007
Araihazar, Site B	30	0.7	200	Stute et al., 2007
Araihazar, Site C	15	5	50	Stute et al., 2007
Araihazar, Site F	15	5	75	Stute et al., 2007
Vietnam, H-transect	55	0.5 [*]	200	Postma et al., 2012
Vietnam, Van Coc	30	0.25 [*]	750	Postma et al., 2012
Vietnam, Phu Kim	15	0.5 [*]	500	Postma et al., 2012
Vietnam, Phung Thuong	15	0.5 [*]	1000	Postma et al., 2012

* The Vogel model was used to estimate vertical velocities in Araihazar. Velocities reported in Postma et al. 2012 were used, and indicated with an asterisk.

The As depth profiles for other sites were then compared to the results of the idealized flushing model to approximate the extent of flushing.